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Carbon dioxide supercritical fluid extraction of incinerator fly ash with a reactive solvent modifier

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Abstract

Carbon dioxide supercritical fluid extraction was used to extract polycyclic aromatics, halogenated phenols, halogenated aromatics and dioxins from a municipal incinerator fly ash matrix. The extraction solvent was modified with methanol or a reactive solvent modifier, N,O-bis-trimethylsilyl-trifluoroacetamide (BSTFA), which was added to the sample before extraction. Extracts, obtained at two temperatures and with three supercritical fluid formulations, were analyzed by the US Environmental Protection Agency contract laboratory program GC–MS procedure for semi-volatile organic compounds. Average recoveries of surrogate analytes with pure carbon dioxide and carbon dioxide modified with methanol were 50% (500 atm and 100°C). Average recoveries were 82% at 100°C and 54% at 30°C with BSTFA present. Carbon dioxide modified with methanol was found to be less efficient than carbon dioxide modified with BSTFA. Unlike earlier uses of reactive modifiers, the acidic and phenolic components were determined as the free acids and phenols. Hydrolysis of trimethylsilyl derivatives of phenols, produced by the modifier during the extraction, with methanol reproduced the free phenols. At 60°C the average hydrolysis yield of the four phenols was 96.7%. This hydrolysis step also allowed analysis of free acids by standard methods.

1. Introduction

The advantages of supercritical fluid extraction (SFE) are listed elsewhere [1], but primarily include speed and reduced solvent waste. Solvents used in SFE are gases at room temperatures and pressures. This simple fact gives SFE a great speed advantage over conventional liquid extraction techniques. Extracts produced by liquid methods using solvents such as methylene chloride must be concentrated from hundreds of milliliters to just a few milliliters. This requires time, provides an opportunity for analyte loss and release of chlorinated solvent into the atmosphere and produces waste solvent. The supercritical solvents which are gases at standard temperatures and pressures are easily removed from the extract at room pressure. However, solvents such as carbon dioxide enable extraction of only non-polar and weakly adsorbed compounds.

A major limitation of SFE is its inability to

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extract polar and strongly adsorbed analytes. Common SFE solvents, like carbon dioxide, lack the intermolecular cohesive solvent strength needed to overcome the energy of adsorption binding the analyte to the sample matrix. One technique used to increase the solvent strength of the supercritical fluid is to introduce small amounts of polar solvent modifiers to the extracting solvent [2,3]. Polar modifiers act in two ways. First, the overall polarity of the extraction solvent is raised, increasing the solubility of polar analytes in the fluid. Second, the modifier competes with the analytes for the same adsorptive sites to which the analytes are adsorbed. Displacement of the analyte from the sample matrix by the solvent modifier drives the analyte into solution. Presumably the stronger a modifier's affinity with adsorptive sites of the matrix the more pronounced the displacement effect.

The objective of the project was to evaluate the potential of coupling standard US Environmental Protection Agency (EPA) methods such as the EPA contract laboratory program (CLP) gas chromatography with mass spectral detection (GC–MS) method for semi-volatile compounds with SFE using the reactive modifier approach for the determination of organic compounds from highly adsorptive matrices such as municipal incinerator fly ash. To achieve this objective, the experiments were divided into three phases.

Because the use of reactive modifiers produces derivatized analytes and the EPA CLP GC–MS method for semi-volatile compounds was designed for underivatized compounds, phase I of the project tested a collection method in which derivatized analytes were hydrolyzed back to their original form before GC–MS analysis. Phase II of the project compared the extraction efficiencies of pure supercritical carbon dioxide, carbon dioxide modified with methanol and carbon dioxide modified with a derivatizing reagent at both high (100°C) and low (30°C) temperatures. Finally phase III: identification and quantification of native compounds by the EPA CLP GC–MS method for semi-volatile compounds.

2. Experimental

2.1. Instrumentation

Supercritical fluid extractor

The extractor was purchased from ISCO (Lincoln, NE, USA) and consisted of a syringe pump (Model 260D) and a stainless-steel extraction unit (Model SFX 2-10) with heating block and two extraction cells. Each extraction cell consisted of a metal tube with an internal volume of 10 ml and was capped at both ends with threaded stainless-steel caps containing 2-μm stainless-steel frit filters. The extraction cells were held at the extraction temperature within an aluminum heating block. Pressure was maintained in the extraction cells with a deactivated 20 cm × 50 μm I.D. fused-silica capillary flow restrictor and a partially opened exit valve. The low pressure end of the restrictor was placed in a solvent trap containing 0.5 ml methanol. The solvent trap has been described elsewhere [4].

Gas chromatography–mass spectrometry

The GC–MS system used in these experiments was that recommended by the EPA CLP method. It consisted of a Hewlett-Packard 5890 gas chromatograph fitted with a 5970 mass-selective detector.

Chromatographic operating conditions for all experiments in this project were as follows: The chromatographic column was a 30 m Rtx-5 fused-silica capillary column (Resteck, Bellefonte, PA, USA). The carrier gas was helium at 1 ml/min. All separations were temperature programmed with an initial column temperature of 40°C with no hold time. The oven was programmed from 40 to 270°C at 10°C/min with a final hold of 35 min. The injection port temperature was maintained at 270°C.

Operating conditions for the mass spectrometer were as follows: the ion source for the mass selective detector was held constant at 250°C. The voltage for the electron impact ion source was operated at 70 V, but was not turned on until the solvent and reagent byproducts had eluted from the chromatographic column, 8.5 min after

injection. For some samples the detector was operated in the scanning mode, for others it was operated in a selective ion monitoring mode.

Gas chromatography–flame ionization detection

Determinations concerning phase I of this project, the hydrolysis of the extracted derivatives, were made on a chromatograph identical to the one described above but fitted with a flame ionization detector. Identifications were made by matching retention times with those of standards.

2.2. Experimental procedures

The project was divided into three phases: hydrolysis of trimethylsilyl (TMS) derivatives, extraction of surrogate analytes, and, finally, the extraction and analytical determination of several native organic compounds in municipal fly ash. Experimental procedures for each phase of the project are given below.

Phase I: Hydrolysis of TMS derivatives

To determine if TMS derivatives of semi-volatiles could be quantitatively converted to their underivatized form upon collection from the supercritical fluid extractor, a mixture of surrogate compounds were derivatized and then collected and hydrolyzed upon collection in methanol. The test mixture used in this phase of the project included 1 μg/μl each of the following eight compounds dissolved in methylene chloride: 2-fluorophenol (2FP), phenol-d_5 (PHL), 2-chlorophenol (2CP), dichlorobenzene-d_4 (DCB), nitrobenzene (NBZ), 2-fluorobiphenyl (FBP), tribromophenol (TBP) and terphenyl-d_{14} (TPH). A "d" at the end of a compound name indicates that the compound was deuterated, the number at the "d" is the number of protons replaced. A 10-μl aliquot of this 1 μg/μl test mixture was placed in a 0.5-ml quantity of trap solvent methylene chloride and treated with 100 μl of the neat commercial grade derivatization reagent N-O-bis trimethylsilyl-trifluoroacetamide (BSTFA) (Pierce, Rockford, IL, USA). Derivatization was conducted for 15 min at 80°C. After derivatization, the 0.5-ml aliquot of the sample was diluted to 2.0 ml with methanol to simulate the collection process. The process described above resulted in methanol solutions of the hydrolyzed surrogate compounds at the 4 μg/μl level.

These hydrolyzed solutions were analyzed by GC–flame ionization detection (FID) by making a 1-μl splitless injection of the extract. The complete derivatization, hydrolysis and analysis steps were repeated three times at different temperatures to obtain the data presented in Table 1.

Phase II: Extraction of surrogate analytes

The extraction efficiency of the three solvents was compared for the extraction of a mixture of test compounds from a municipal fly ash matrix. The three solvent formulations compared were (1) pure supercritical carbon dioxide, (2) supercritical carbon dioxide modified with methanol and (3) supercritical carbon dioxide modified with a derivatizing reagent. The test mixture was the same as that used for the hydrolysis studies and corresponded to the surrogate analytes required in the EPA CLP method for the extraction of semi-volatiles from solid matrices. They were the same as listed in phase I. The municipal fly ash sample was from the municipal waste incinerator, Toronto, Canada and was obtained in bulk from samples collected by

Table 1
Derivatization and hydrolysis yields of surrogate analytes

Compound	Yield (%) at		
	25°C	60°C	80°C
2FP	96	95	96
PHL	62	83	87
2CP	95	95	95
DCB	98	96	97
NBZ	97	95	95
FBP	99	98	91
TBP	100	101	101
TPH	106	112	111

Professor K.W. Karasek and Dr. K.P. Naikwadi of the University of Waterloo, Waterloo, Canada.

Pre-extraction treatment

The procedure for all of the extractions was the same. A 6-g sample of fly ash was loaded into a 10-ml extraction cell. Then, the surrogate compounds were added to the sample matrix in two mixtures, base-neutrals (1,2-dichlorobenzene-d_4, nitrobenzene-d_5, 2-fluorobiphenyl and terphenyl) at a concentration of 1 μg/μl for each compound and acids (2-fluorophenol, phenol-d_5, 2-chlorophenol-d_4 and 2,4,6-tribromophenol) at a concentration of 1.5 μg/μl for each compound. After application of the surrogate analytes, 10 μl of each solution, the solvent was allowed to evaporate at room temperature for fifteen minutes before the extraction cell was sealed or modifiers were added.

Modifiers for the extractions were added as liquids directly to the fly ash samples. When methanol was the modifier, 500 μl of pure methanol were injected onto the fly ash sample. When neat BSTFA was the modifier, 250 μl of the commercially purchased solution were injected. Additions of larger volumes, 500 and 750 μl, made no significant difference in extraction efficiency. After the addition of the modifier, the sample cell was sealed and pressurized to 500 atm (1 atm = 101 325 Pa) with pure carbon dioxide.

Extraction

The extraction process was a two-step procedure. First, a static extraction was conducted for 5 min at 500 atm and at 30 or 100°C. This initial static extraction period was followed by a dynamic extraction in which carbon dioxide flowed through the cell at a rate of 0.1–0.3 ml/min measured at the pump. At this rate, approximately four cell volumes of the solvent were passed over the sample in a 3- to 4-h extraction. A partially opened exit valve was used to retard and control and carbon dioxide flow. This low flow-rate was required in order to achieve a high trapping efficiency.

Sample collection

The analyte trap contained 1 ml of a methanol–methylene chloride (3:1, v:v) mixture into which the fused-silica capillary restrictor was placed such that the supercritical carbon dioxide was depressurized in the solution, depositing the analytes in solution. If required, the trapping solvent could be heated after collection to insure quantitative conversion of the derivatives to their underivatized form. During the sample collection process, some of the trapping solvent was evaporated. After extraction, methylene chloride was added to bring the volume back to 1.0 ml.

Internal standards

In addition, 5 μl of an internal standard solution were added to the 1.0 ml extract solution. The internal standard consisted of 1,4-dichlorobenzene-d_4, naphthalene-d_{10}, acenaphthene-d_{14}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} at concentrations of 4 μg/μl for each component. Thus, the final concentration of each 1.0-ml sample extract was 20 ng/μl of each standard. The extract was then transferred to the auto sampler where 2-μl injections were made into the GC–MS system with no further preparation.

Phase III: Extraction of native analytes

Identification of the native analytes which were adsorbed onto the fly ash was accomplished as described in EPA CLP Semi-Volatile Method. Target components were also quantified by the internal standard method. A list of the internal standards is given in the section above. The target compounds, internal standards, and surrogates were identified by direct comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Before an analyte identification was verified, two criteria were satisfied: The analyte eluted from a GC at the same relative retention time as the standard and the mass spectrum of the analyte matched that of the standard.

3. Results and discussion

Recently we proposed that stronger affinity with the matrix active sites can be achieved if the modifier reacts with, rather than simply adsorbs to, the surface [4,5]. The addition of chemical reagents to the extraction solvent to act as reactive solvent modifiers has been used to extract several matrices. Reactions employed thus far are silylation [5], and methyl esterification [3]. This laboratory has shown silylation reagents are applicable to the extraction of polar and acidic compounds from biological samples, sediments and air particulates. Conversion of polar analytes, such as fatty acids and diacids, to the silyl derivatives during the extraction rendered them more soluble in the non-polar extraction fluid. The non-polar derivatized analytes were readily extracted and determined by GC. Interestingly, compounds that were inert to the derivatization reagent also benefited from the presence of the reagent. This benefit arose from the action of the reagent on the matrix. Compounds adsorbed by hydrogen bonding to the matrix surface was released when the surface moiety was converted to the TMS derivative. The strength of a hydrogen bond is about one tenth that of a covalent bond. Thus the displacement of the adsorbed molecule by a covalently bonded TMS group was energetically favored over temporary and weaker displacement by non-reactive modifiers.

While the first approach, the addition of polar modifiers, has been investigated extensively for both SFE and supercritical fluid chromatography, the second approach, the addition of reactive modifiers, has been used in the extraction of only a few matrices such as coffee beans, tea, marine sediment, agricultural soil, airborne particulate matter and sewage sludge. All of these studies have involved matrices which could be classified as moderately polar. Fly ash from incinerators, however, is a highly adsorptive and oxidized matrix and is difficult to extract using pure supercritical carbon dioxide or even supercritical carbon dioxide with polar modifiers. The difficulty of extracting municipal incinerator fly ash has been demonstrated. In these studies matrix destruction with acid treatment was required for extraction of chlorinated dibenzo-*p*-dioxins and dibenzofurans [6].

3.1. Phase I: Hydrolysis of TMS derivatives

Simultaneous supercritical fluid chemical derivatization and extraction (SFDE) normally has been followed by analysis of the target analytes as their derivatives. However, standard analysis methods, such as EPA CLP method employed in this work, are often designed to determine the underivatized analyte. For example, the EPA CLP method used in this work is designed to monitor free phenols or acids rather than the TMS derivatives of these compounds. Thus, in order to use the EPA CLP method, an easy, quantitative conversion of the extracted analyte back into the native compound was needed. This was achieved by simply collecting the derivatized extract in methanol. Methanol hydrolysed TMS esters back to free acids and phenols during the collection of the extract.

Fig. 1a shows a total ion chromatogram for the test mixture of surrogate compounds, demonstrating retention times of these underivatized compounds. Fig. 1b shows a typical chromatogram for this mixture after derivatization with BSTFA. From these two chromatograms, it was clear that the derivatization process was nearly quantitative. Peaks for 2FP, PHL, 2CP and TBP are missing in Fig. 1b compared with Fig. 1a. Instead, four new peaks appear in Fig. 1b which correspond to the TMS derivatives of these four phenolic compounds. It was interesting to note the effect that the derivative had on chromatography. The TMS-2FP derivative eluted faster than its underivatized analogue while the derivatives of the other three phenols eluted later than their underivatized counterparts. Those test compounds which do not form derivatives, DCB, NBZ, FBP and TPH, occurred at the same elution time in both chromatograms. Note that in Fig. 1b, the relative sensitivity of the derivatized compounds is greater than the underivatized compounds. This is one advantage of derivatiza-

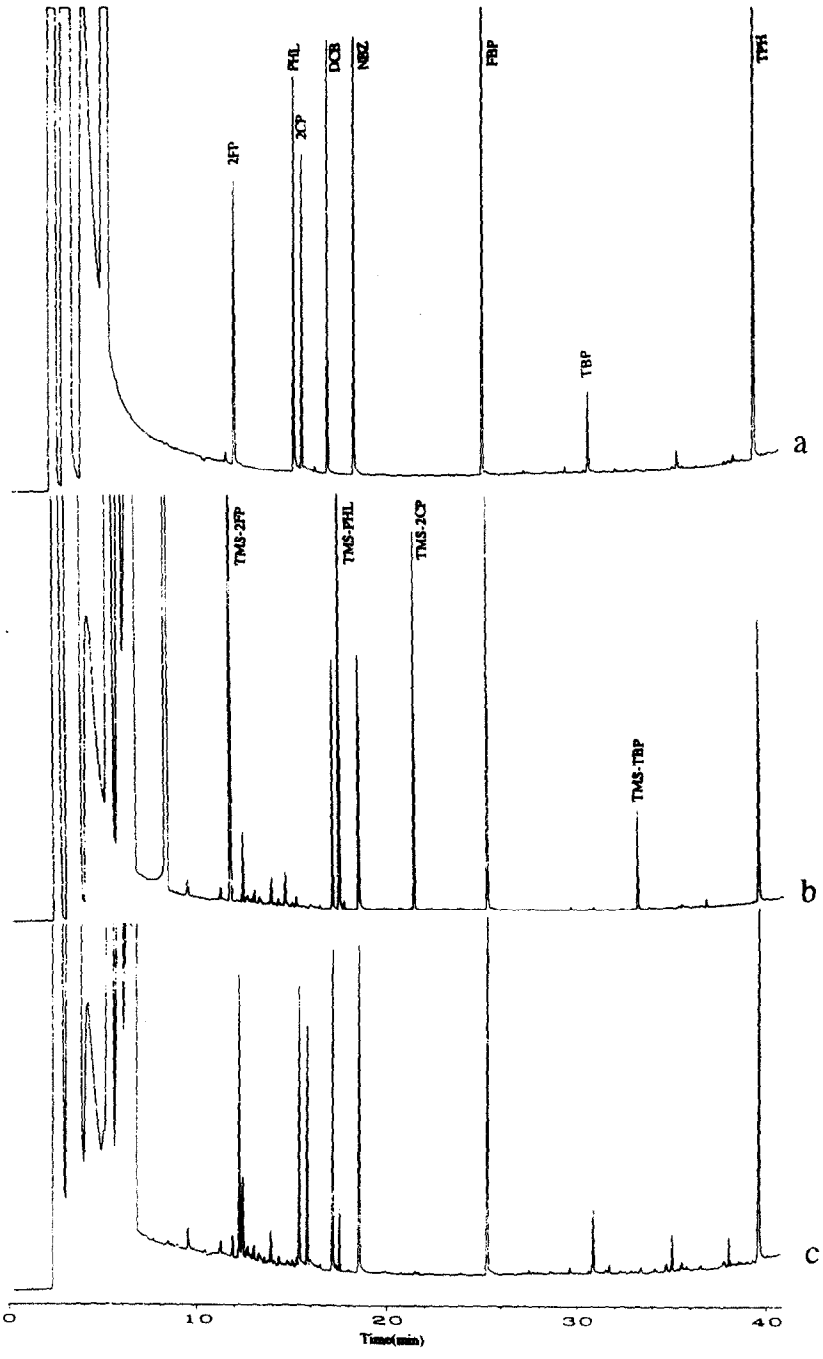

Fig. 1. Gas chromatograms of surrogate analytes. The original eight compounds: 2-fluorophenol (2FP), phenol-d_5 (PHL), 2-chlorophenol (2CP), dichlorobenzene-d_4 (DCB), nitrobenzene (NBZ), 2-fluorobiphenyl (FBP), tribromophenol (TBP), terphenyl-d_{14} (TPH) are seen in the top trace (a). The middle trace (b) is the same mixture after treatment with BSTFA. The label "TMS" indicates the trimethylsilyl derivative of the analyte. The bottom trace (c) is the derivatized mixture after hydrolysis with methanol. Analysis conditions: 1-μl splitless injection of the extract was made on to a 30 m Rtx-5 capillary column held at 40°C. The column temperature was raised at 10°C/min to 270°C where it was held 35 min.

tion, but requires that the method be calibrated for the derivative rather than the native compound. Thus, in order to conform to previously described methods, the derivatives were hydrolyzed back to the native compound for detection as shown in Fig. 1c. In this third chromatogram, the native peaks reappear and the chromatogram resembles that of Fig. 1a. Table 1 presents the results of the hydrolysis experiments. At all temperatures the hydrolysis, except for PHL, was better than 90% complete.

3.2. Phase II: Extraction of surrogate analytes

Use of surrogate compounds to spike the fly ash matrix was not anticipated to render information on how well native compounds might be desorbed from the matrix but was expected to provide information on the efficiency at which desorbed compounds were removed from the extraction cell and trapped in the collection cell. In addition, they provide information on sample loss due to irreversible adsorption and other losses during the extraction process. Fig. 2 shows the GC–MS reconstructed ion chromatograms of the fly ash extract produced at 500 atm and 100°C with pure carbon dioxide (Fig. 2a), carbon dioxide with methanol (Fig. 2b) and carbon dioxide with BSTFA (Fig. 2c).

Table 2 compares the recoveries found for each of the surrogate compounds after extraction with pure carbon dioxide, methanol modified carbon dioxide and BSTFA modified carbon dioxide. It is interesting to note the trend in the extraction efficiency of the pure carbon dioxide. With the exception of nitrobenzene, extraction efficiency decreases as the elution time of the analyte increases (analytes are listed in order of increasing chromatographic elution time). This indicates that the extraction efficiency of pure supercritical carbon dioxide was determined primarily by the vapor pressure of the analyte. This trend is less noticeable with the methanol modified extraction and is not seen in the BSTFA-modified extraction. One explanation was that compounds with higher heats of vaporization, greater cohesive energy between themselves and the matrix surface, were adsorbed to the surface more strongly. Supercritical carbon dioxide could not overcome this adsorption energy. Methanol could disrupt the matrix-analyte cohesion and thus desorbed the compounds to some extent. BSTFA completely displaced these compounds from the surface; it was able to overcome the adsorptive forces.

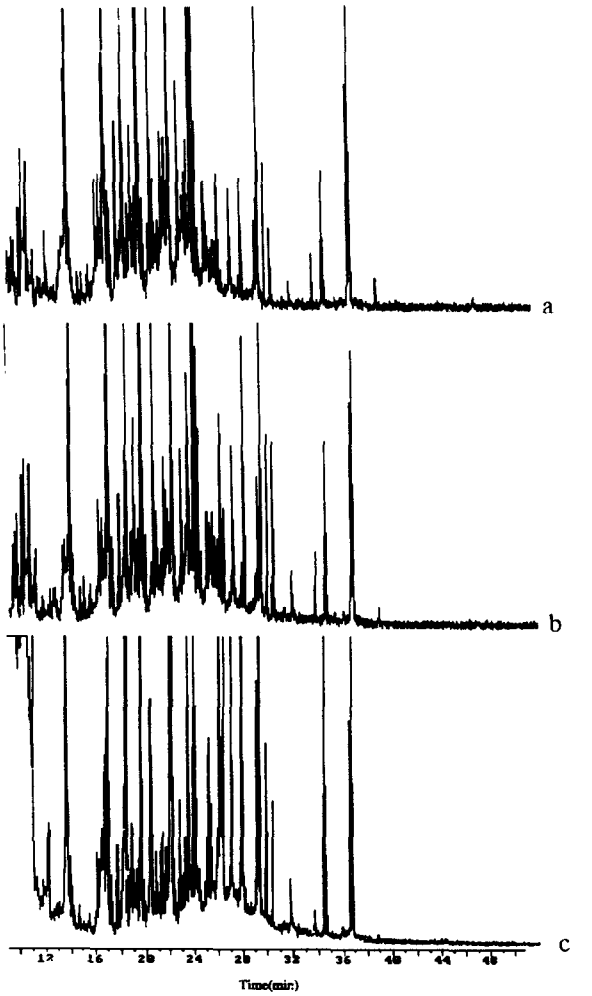

Fig. 2. Gas chromatograms of fly ash extract. Extraction conditions: 30°C, 500 atm, carbon dioxide with 250 μl BSTFA. Analysis conditions: 2-μl splitless injection of the extract was made on to a 30 m Rtx-5 capillary column held at 40°C. The column temperature was raised at 10°C/min to 270°C where it was held 35 min.

Table 2
Recoveries of surrogate analytes from municipal incinerator fly ash matrix

Compound	Recovery (%)			
	CO_2, 100°C	CO_2 with MeOH, 100°C	CO_2 with BSTFA	
			30°C	100°C
PHL	69 (11)[a]	80 (4)	46 (10)	100 (3)
2CP	65 (3)	35 (1)	61 (7)	86 (20)
DCB	69 (12)	55 (21)	89 (16)	102 (4)
NBZ	38 (53)	5 (3)	48 (3)	103 (5)
FBP	75 (7)	62 (26)	32 (1)	116 (5)
TBP	35 (19)	62 (14)	40 (40)	48 (17)
TPH	27 (9)	4 (2)	31 (6)	106 (2)
Average	54 (20)	43 (10)	50 (12)	94 (8)

[a] Values in parentheses are % relative standard deviations.

3.3. *Phase III: Extraction of native analytes*

A problem in extraction studies for trace organic analysis is that spiked analytes do not necessarily mimic the adsorptive behaviour of native analytes. Native analytes which have been "weathered" often do not behave in the same manner as their spiked standards. In this section of the study, twelve native compounds were identified on the fly ash and their extraction yields were compared for the three solvents. These semi-volatile analytes were identified in the fly ash extracts following qualitative procedures used in EPA CLP methods and are listed in Table 3. At these low levels (ng/g), isomers of the dichlorobenzenes and the trichlorophenols could not be identified separately with certainty.

Quantitative data for each of these compounds

Table 3
Native compounds identified in municipal waste incinerator fly ash

Compound	ng/g			
	CO_2, 100°C	CO_2 with MeOH, 100°C	CO_2 with BSTFA	
			30°C	100°C
Phenol	nd	32	43	110
Dichlorobenzenes	75	140	120	170
N-nitroso-di-N-propylamine	68	24	130	300
1,2,4-Trichlorobenzene	110	190	110	56
Benzoic acid	22	320	37	96
4-Methyl naphthalene	nd	10	30	37
Trichlorophenols	nd	59	nd	450
Acenaphthylene	77	54	20	101
Acenaphthene	nd	77	37	150
N-nitrosodiphenylamine	nd	29	20	47
Dibenzofuran	nd	nd	nd	13
Hexachlorobenzene	36	46	46	170

nd = Not detected.

are given for each extraction method. With pure carbon dioxide as the extraction solvent, no native phenols were detected in the sample. However, when methanol was added to the sample as a modifier, both phenol and the trichlorophenols were found. When BSTFA was used as the modifier, a several fold increase in extraction efficiency over the methanol modified extraction was observed for several compounds. Of the twelve native compounds identified, ten showed significantly better extraction yields when BSTFA was used as the modifier. This was not the case for 1,2,4-trichlorobenzene and benzoic acid. These compounds were extracted better with the methanol modified solvent. In addition to this seemingly contradictory evidence, relative standard deviations for the BSTFA extraction of these two compounds were the highest observed in this study, 140% for 1,2,4-trichlorobenzene and 100% for benzoic acid. Other relative standard deviations for the native analytes at the ng/g level ranged from 1% for acenaphthylene to 84% for phenol and dibenzofuran.

On the whole, however, the evidence is relatively clear that native compound extraction was more efficient with BSTFA than with methanol or pure carbon dioxide although extraction precision was not as high as we have come to expect with the more traditional Sohxlet extraction method.

3.4. Temperature effects

The solvation strength of a supercritical fluid is a function of density. According to Czubryt et al. [7] who used an argument based on Hildebrand solubility parameters (see Ref. [8]), the more dense and liquid-like the more solvation power the fluid has. That is, at lower temperatures the fluid could more readily overcome the affinity an adsorbed molecule has for the surface to which it is adsorbed. However, adsorbed molecules can overcome the energy barrier and desorb from a surface by thermal energy. Increasing the extraction temperature would decrease the density of the extraction fluid but at the same time give adsorbed molecules more thermal energy to overcome the desorption energy barrier. These two views would seem to be at odds with each other. Extractions were made at two temperatures, 30°C (1.0 g/ml) and 100°C (0.80 g/ml), to determine if solvent strength or temperature controlled yields from this matrix.

The recoveries of the surrogates, Table 2, implied that the surrogates adsorbed irreversibly to the fly ash matrix at 30°C while at 100°C they eluted with much less adsorption. Concurrently, the yields at the higher temperature also suggest that it is the better extraction temperature. The total yield of quantified compounds in the 100°C extraction was determined to be 1.7 μg compared to a total yield of 0.60 μg for the 30°C extract. Although not conclusive, it appears that the higher temperature not only desorbs native compounds better but might also prevent the surrogates from adsorbing. The higher thermal energy is postulated to prevent the native analytes from readsorbing once solvated in the extraction solvent. The solvation strength view of supercritical fluid extraction does not address adsorption of analytes.

3.5. Chlorinated dioxins

Although these experiments were not designed to determine chlorinated dioxins, the presence of several dioxin precursors (dichlorobenzenes, trichlorobenzene and trichlorophenols) in the fly ash suggested that dioxin may also be present. However, even though chlorinated dioxins are known to form on the surface of fly ash after combustion [9], no dioxins were detected in the extracts when the mass spectrometer was operated in its less sensitive scanning mode. To increase sensitivity, single ion monitoring was used to produce the selective chromatograms shown in Fig. 3. Fig. 3a shows the selective ion chromatogram of m/z 322 that is the molecular ion for tetrachloro-dibenzo-dioxin. Five peaks can be seen in the chromatogram. The identities of the two peaks with retention times of around 27 min were confirmed as two TCDD isomers by a second selective ion chromatogram. Fig. 3b shows this m/z 257 ion chromatogram. This mass corresponds to the molecular ion minus COCl

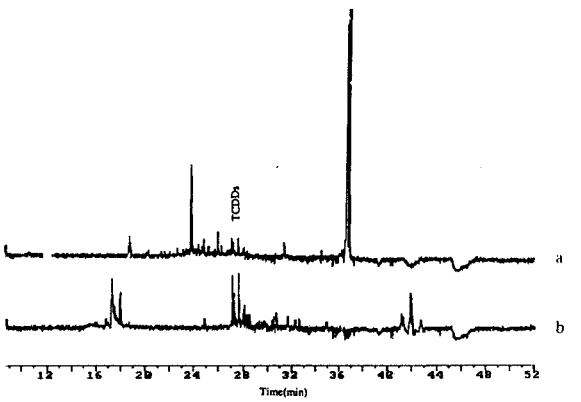

Fig. 3. Selective ion chromatograms of tetrachlorodioxins (TCDDs). (a) Selective ion chromatogram of the M^+ ion at m/z 322. Selective ion chromatogram for the $(M - COCl)^+$ ion at m/z 257. Chromatographic and analysis conditions as in Fig. 2.

(M − 63). The relative intensities of the two ions are consistent with mass spectra of these compounds [10].

Although quantitative data were not obtained for these compounds, it is encouraging that these compounds were observed when BSTFA was used with supercritical fluid extraction even though the ash was not pretreated with HCl before extraction and no clean-up procedures were used after extraction to decrease chemical noise. Pure carbon dioxide or carbon dioxide modified with methanol is generally not sufficient to extract chlorinated dioxins unless the ash has been treated with HCl to remove heavy metals prior to extraction.

4. Conclusions

The use of a derivatizing reagent, such as BSTFA, as an additive to solid samples, even highly reactive samples such as municipal incinerator fly ash, enhanced the extraction efficiency of supercritical carbon dioxide for the many semi-volatile compounds extracted from these matrixes. For analytes which form silyl derivatives, this enhancement in extraction efficiency is attributed to both the higher solubility of the derivatives in supercritical carbon dioxide and the disruption of the analyte–matrix interaction by derivatization. For semi-volatile compounds, which do not form silyl derivatives, disruption of the analyte–matrix interaction enhanced extraction efficiency as well. By collecting silylated analytes in a solvent of methanol after SFE, silyl derivatives are converted back to their native form. The extracts can then be analyzed by standardized procedures such as the EPA CLP method for semi-volatile compounds. The effect of temperature on extraction efficiency was found to be significant and as effective as the solvent conditions investigated.

Acknowledgements

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